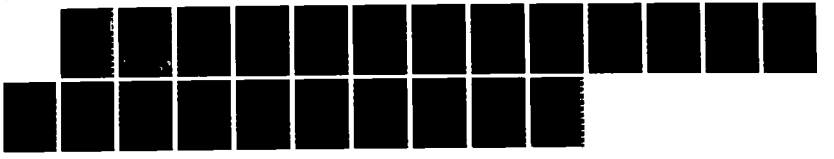
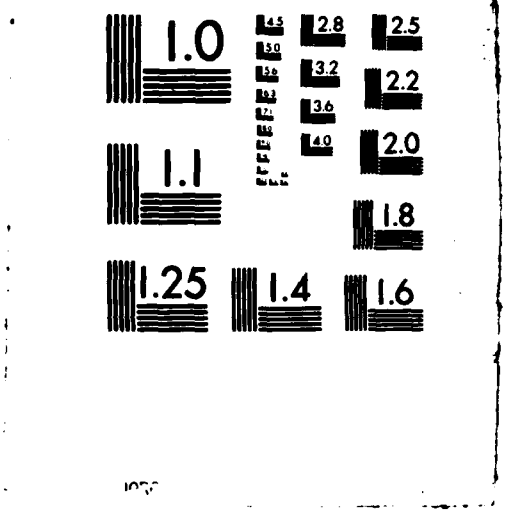
AD-A172 283 CONDENSATION POLYMERS WITH CONTROLLED STRUCTURE(U) 1/1
MASSACHUSETTS INST OF TECH CAMBRIDGE DEPT OF CHEMICAL
ENGINEERING U W SUTER ET AL. 04 AUG 86

UNCLASSIFIED N00014-85-K-0161 F/G 11/9 NL




1.0
1.1
1.25
1.4
1.6
1.8
2.0
2.2
2.5
2.8
3.2
3.6
4.0
4.5
5.0

(12)

Report

CONDENSATION POLYMERS WITH CONTROLLED STRUCTURE

AD-A172 283

Ulrich W. Suter
Werner R. Meyer
Frank T. Gentile
Department of Chemical Engineering
Massachusetts Institute of Technology
Room 66-456
Cambridge, MA 02139

4 August 1986

Annual Report for the Period 85AUG01 to 86JUL31
Contract Number N00014-85-K-0161

NR 413c 003

DTIC FILE COPY

Distribution		
Scientific Officer	N00014	1
Administrative Contracting Officer	N66017	1
Director, Naval Research Laboratory	N00173	6
Defense Technical Information Center	S47031	12

Prepared for
OFFICE OF NAVAL RESEARCH
800 North Quincy Street
Arlington, Virginia 22217

This document has been approved for public release and sale; its distribution is unlimited.

DTIC ELECTE SEP 30 1986 S D E

86 8 11 022

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE *(and Subtitle)* Condensation Polymers with Controlled Structure		5. TYPE OF REPORT & PERIOD COVERED
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Ulrich W. Suter		8. CONTRACT OR GRANT NUMBER(s) N00014-85-K-0161
9. PERFORMING ORGANIZATION NAME AND ADDRESS Massachusetts Institute of Technology		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research 800 Quincy Street Arlington, Virginia 22217		12. REPORT DATE 86 AUG 4
		13. NUMBER OF PAGES
14. MONITORING AGENCY NAME & ADDRESS *(if different from Controlling Office)*		15. SECURITY CLASS. *(of this report)*
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT *(of this Report)*

Scientific Officer	N00014 (1)	Director, Naval Research Laboratory	N00173 (6)
Administrative Contracting Officer	N66017 (1)	Defense Technical Information Center	S47031 (12)

17. DISTRIBUTION STATEMENT *(of the abstract entered in Block 20, if different from Report)*

18. SUPPLEMENTARY NOTES

19. KEY WORDS *(Continue on reverse side if necessary and identify by block number)*

20. ABSTRACT *(Continue on reverse side if necessary and identify by block number)*

The polymerization procedure that had been used in the first year of funding was improved dramatically during the current period. A homogenous condensation system for the modified Schotten-Baumann reaction at ambient temperatures has been found (NMP:THF = 10:1, +3%w/w LiCl) that routinely yields polymers with a degree of polymerization sufficient to form fibers ~~(η_{inh} = 3-5 dl/g)~~ and that allows for the slow addition of one of the reagents to the others without side reactions. We have now synthesized poly(2,6-dichloro-p-phenyleneterephthal-

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE *(When Data Entered)*

Block 20 (continued)

amide), poly(2-nitro-p-phenyleneterephthalamide), and poly(2-methoxy-p-phenyleneterephthalamide) with the new system. It has been determined, both theoretically and experimentally, that they form liquid crystalline solutions at concentrations similar to those of the non-substituted polymer (i.e., "Kevlar"). Thus far, poly(2,6-dichloro-p-phenyleneterephthalamide) has been synthesized in ordered and random forms and we are devising new NMR techniques to quantitatively determine this order. Solubility differences between the ordered and the random chains are striking.

Accession For
NTIS GRA&I X
DTIC TAB
Unannounced
Justification ltr per
By
Distribution/
Availability Codes
Dist | Avail and/or Special
A-1

QUALITY INSPECTED 1

Annual Report for the Period 85AUG01 to 86JUL31
4 August 1986

Summary

This project's objective is to develop new rigid-rod polyamides with a controlled and pre-selectable degree of constitutional regularity. The reason behind this approach is the fact that condensation polymers that contain units whose mutual orientation in the chain can be distinguished give rise to constitutional isomerism similar to the "head/tail" isomerism in vinyl polymers. Regular polymers are characterized by structures containing either only "head-to-head/tail-to-tail" or only "head-to-tail" structures. This isomerism has been found to influence the properties of many polycondensates significantly, and it is anticipated that the processability of extended-chain rigid-rod polyamides will be greatly improved.

Acknowledgements

Lively and helpful discussions with Dr. Stephanie Kwolek of CR&D of E. I. DuPont de Nemours and Co. and with Professor Piero Pino from the ETH in Zürich are gratefully acknowledged. Without the services of the Chemistry Analytical Laboratory and the Materials Research Laboratories at MIT we certainly could not perform the work we are carrying out.

Table of Contents

1. Introduction
2. Polymers Synthesized
   - 2.1 General
   - 2.2 Synthetic Techniques
   - 2.3 Properties of Polymers with Controlled Constitution
3. Monomer Preparation
   - 3.1 General
   - 3.2 Synthetic Techniques
   - 3.3 Determination of Reactivity Ratios
4. Polymer Characterization
   - 4.1 General
   - 4.2 Rigid Rod Behavior
   - 4.3 Analysis of the Liquid Crystalline Phase
   - 4.4 Instrumental Techniques
5. Conclusions and Recommendations
6. References
7. Appendix
   (from Polymer Preprints, ACS Meeting in Anaheim, 1986)

Annual Report for the Period 85AUG01 to 86JUL31
4 August 1986

1. Introduction

Extended-chain rigid-rod polymers, foremost among them the wholly aromatic polyamides (aramides), have extraordinary properties as fibrous materials: their specific moduli and specific strength are often on a par with those of all other known fibers and their thermal stability is excellent [1]. Thus they are used in many applications requiring extraordinary mechanical performance. They might conceivably be equally attractive in other forms, e.g. as bulk materials, films, etc., but are not conveniently processable, and the only practical transformation to date is, to our knowledge, solution spinning to fibers.

The desirable properties of aramides probably originate in their rigid-rod character which forces solutions of modest concentrations to be liquid crystalline and hence, allows for easily achievable high orientation in an extentional flow. The undesirable characteristics, i.e. insolubility in convenient solvents and extremely high softening temperature, are probably due to the high degree of crystallinity and the ensuing extensive "hydrogen-bonding." The work performed under this contract is aimed at developing new extended-chain rigid-rod aramides that retain the desirable characteristics, i.e. display very high axial ratios and, at the same time, cannot crystallize in the traditional sense. We hope this can be achieved by introduction of a well controlled degree of constitutional disorder into the chains.

The constitutional isomerism exploited here is of an orientational type, similar to the "head/tail"-type isomerism in vinyl polymers that has been explored for sixty years. (In vinyl polymers, ironically, it essentially cannot be controlled and is overshadowed in its effects by the influence of tacticity). In condensation polymers this type of structural order is perfectly controllable, and its effects are substantial [2]. At present no molecular theory of the properties of condensation polymers exists and the mechanisms by which properties differ with respect to structure are largely unknown but, we conjecture that crystallinity and intermolecular cohesion are both important factors. The constitutionally regular aramides we prepare should be able to merge into crystalline domains and form many "hydrogen bonds" while the more random chains should have difficulty crystallizing and be "less cohesive." The relative sizes of the groups that give rise to the isomerism have large affects in both the solid and liquid crystalline phases [1,3]. All chains, the regular as well as the irregular ones, have very high axial ratios and form anisotropic solution phases (liquid crystalline

domains) in which the macromolecules are aligned relative to each other. (This spontaneous development of order seems to be responsible for the very high crystallinity and orientation in the fibers formed from anisotropic solutions and seems to be a major cause for the excellent thermal and mechanical properties of aramides [1,3].)

We have prepared a range of modified aramides from non-symmetric monomers. We have begun to see that we can control the crystallinity of these polymers, which we believe to be the main cause of their undesirable properties, without affecting their rigid-rod character (the ability to form liquid crystalline solutions) which we conjecture to be the main cause of their desirable properties. The following sections deals with the polymers most recently synthesized, new monomers that have been prepared, and advances in the characterization of these polymers.

2. Polymers Synthesized

2.1 General

We have recently synthesized three new modified aramides with new monomers possessing very high reactivity differences. They are:

poly(2,6-dichloro-p-phenyleneterephthalamide) (I)
poly(2-nitro-p-phenyleneterephthalamide) (II), and
poly(2-methoxy-p-phenyleneterephthalamide) (III).

Thus far, polymers II and III have been prepared only with a random constitution, while polymer I has been synthesized in both, random and ordered forms. Order was changed by variations in the monomer feed rates.

2.2 Synthetic Techniques

During the first funding period, several methods of synthesis had been explored, and a Schotten-Baumann procedure using an amide solvent mixture (HMPT:NMP = 2:1) had been selected. Synthesis seemed to proceed smoothly in all cases, but we became suspicious of the method when the inherent viscosities of the samples did not seem to ever exceed ca. 0.3 dl/g (at concentrations of 0.5 g/dl), a value that corresponds to chain lengths too short to allow for the drawing of fibers (the rule-of-thumb states that $\eta_{inh} > 3$ dl/g is required for that). Closer inspection of the reaction system together with a series of model reactions revealed that a reaction of the aromatic acid chloride with the solvent occurs at a sufficiently high rate to severely limit the range of the polycondensation reaction that could be carried out. For example, terephtaloyl chloride readily reacts with hexamethylphosphortriamide (HMPT), N-methylpyrrolidone (NMP), and dimethlyacetamide (DMAC). (The industrial systems employ rapid addition of the solid acid chloride and avoids this problem, but all possibility for control of the constitution of the chains is consequently relinquished). During the first funding period a new experimental solvent (tetramethylmethylphosphoramide (TMMP)) had been obtained from DuPont de Nemours and Co., and high hopes had been set on it. However, TMMP reacts even faster with aromatic chlorides than some of the other amide solvents.

We developed a new solvent mixture that allows for slow addition procedures in highly polar solvents without side reactions. In this modified Schotten-Baumann solution method the symmetric acid chloride (YccY) and the non-symmetrical diamine

(XabX) are separately dissolved in totally different solvent systems and then added to one another in a predetermined manner according to the constitution desired. The new system uses tetrahydrofuran (THF) to dissolve the acid chloride and NMP to dissolve the diamine. Lithium chloride (LiCl) is also used to keep the product polymer in solution. When all species have been mixed the solvent system is NMP:THF = 10:1, +3% w/w LiCl. Since the polymerization reaction causes the solution to become very viscous very quickly, NMP is often added to accelerate the reaction to completion.

Polymers I - III were all synthesized with degrees of polymerization (X_n) from 50 to 100. This corresponds to values of η_{inh} of 3 - 5 dl/g (at a concentration of 0.5 g/dl) which is sufficient for the formation of high strength fibers.

Chain constitution was inferred from proton nuclear resonance spectroscopy. Quantitative measurements have proved impossible thus far but qualitative differences in order were clearly perceivable. Better nmr techniques are currently being investigated in order to obtain accurate quantitative information on constitution. Work is in progress on more powerful ^{1}H, ^{13}C, and ^{15}N nmr techniques.

In all, eight different "constitutionally controlled" aramides with 2,6-dichloro, 2-nitro and 2-methoxy moieties on the p-phenylenediamine ring were synthesized. As already stated, constitution was influenced by variations in the feed rates for 2,6-dichloro-p-phenylene diamine to obtain polymer I. Order is denoted by the probability, s, that two non-symmetric p-phenylene diamide units adjacient in the chain point in the same direction, i.e.,

for an ordered constitution (head-to-head/tail-to-tail), $s = 0$,
for a random constitution, $s = 1/2$,
for an ordered constitution (head-to-tail), $s = 1$.

Table 2-1 summarizes the results of the syntheses of these polymers.

TABLE 2-1: "Random" and "Ordered" Polymers Synthesized

Polymer[a]	Process	η_{inh}[b] (dl/g)
P1	XabX and YccY immediately mixed[c]	0.25
P2	XabX and YccY immediately mixed[d]	0.22
P3	XabX and YccY immediately mixed	3.2
P4	XabX and YccY immediately mixed	4.5
P5	XabX and YccY immediately mixed	4.5
P6	YccY added "infinitely" slowly to XabX	4.2
P7	XabX and YccY immediately mixed	5.0
P8	XabX and YccY immediately mixed	4.0

[a] P1: Poly(2,6-dichloro-p-phenyleneterephthalamide) s → 1/2
P2: " s → 1/2
P3: " s → 1/2
P4: " s → 1/2
P5: " s → 1/2
P6: " s → 0
P7: Poly(2-nitro-p-phenyleneterephthalamide) s → 1/2
P8: Poly(2-methoxy-p-phenyleneterephthalamide) s → 1/2

[b] At 30°C, in H_2SO_4 (96%w/w), 0.5 g/dl.

[c] Polymerization carried out using only NMP as a solvent.

[d] Polymerization carried out using only TMMP as a solvent

2.3 Properties of Polymers with Controlled Constitution

Analyses of the solubility, the liquid crystalline character of the solutions in concentrated sulfuric acid, and the thermal characteristics of these polymers were performed. All DSC runs showed thermal stabilities nearly identical to that of an unsubstituted aramide (Kevlar™) synthesized by the interfacial Schotten-Baumann technique. Thus, the excellent thermal stability of Kevlar™ was retained by the substituted polymers. Degradation was observed in all cases with no detectible conventional melt temperature. Future studies on these and other

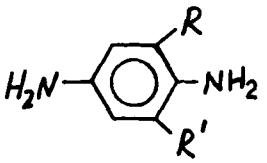
polymers will include thermogravimetric analysis (TGA) in order to quantify the degradation of these polymers.

All substituted polymers are more soluble than Kevlar™. In addition, "random" chloro di-substituted aramides showed greater solubility than "regular" (head-to-head/tail-to-tail) ones. This result agrees with expectations (see Section 1).

3. Monomer Preparation

3.1 General

In order to synthesize polymers with a high degree of order and to have control over this order, the non-symmetric monomer must posses a high difference in reactivity between its two reacting groups. In all our syntheses thus far, the non-symmetric monomer has been a mono-substituted or a 2,6-di-substituted para-phenylenediamine. The relative reactivity of the substituted (to date always slower) side of the monomer (-bX) with respect to the non-substituted (faster) side of the monomer (-aX) is defined as follows:



$$r = k_{bX}/k_{aX}$$

where:
- r = the reactivity ratio
- k_{bX} = the rate constant for the -bX amino group, and
- k_{aX} = the rate constant for the -aX amino group.

The moieties for the p-phenylenediamine are picked such that they are strong electron acceptors or donors and provide large steric hinderance for the ortho amino functional group. Table 3-1 lists the monomers used thus far as well as monomers being studied for future use and their estimated reactivity ratios.

TABLE 3-1: Monomers Synthesized to Date, with Estimated Reactivity Ratio

Monomer	r	
2,6-Dichloro-p-phenylene diamine	1.5×10^{-2}	a
2-Nitro-p-phenylene diamine	7.8×10^{-3}	a
2-Methoxy-p-phenylene diamine		
2-Methyl-p-phenylene diamine	0.5	b
2,6-Dimethyl-p-phenylene diamine	0.1	b

a Estimates of r are based on work performed by Stubbs and Hinshelwood [4].
b Measured by nmr.

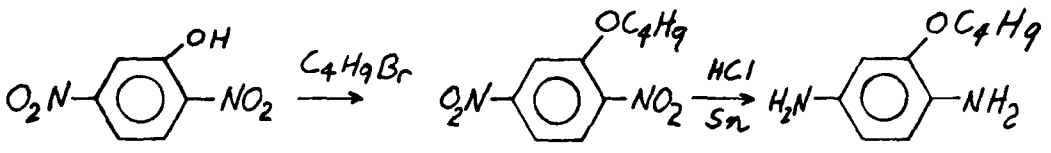
3.2 Synthetic Techniques

The 2,6-dichloro-p-phenylenediamine monomer can be purchased with 97% purity from Polysciences Incorporated. To achieve the 99.9+% purity required for polymerization the monomer is sublimed in vacuo at least twice.

The 2-nitro-p-phenylenediamine monomer is available from Aldrich Chemicals Inc. and is purified by column chromatography followed by vacuum sublimation.

The 2-methoxy-p-phenylenediamine is prepared from the sulfate salt, which is available from Aldrich Chemicals, by neutralizing with an equivalent of base, evaporating the solvent, and vacuum sublimation.

Also commercially available is 2,5-dinitrophenol (from Aldrich Chemicals), an important precursor to a wide range of monomers. After esterification of the hydroxyl group we can reduce the nitro groups to amino functions, purify, and then carry out the polymerization procedure. An example synthesis is shown below.



3.3 Determination of Reactivity Ratios

Reactivity ratios of the two amino functions in the non-symmetric diamines are determined by a competitive amidation of an excess of the diamine with (monofunctional) benzoic chloride, after rapid mixing. The quantitative ratio of the products reflects the kinetic reactivity ratio, r, of the functional groups. The system is otherwise a close as possible to polymerization conditions. (Care must be taken to avoid any side reactions and an acid scavenger is present to avoid effects of increasing acidity of the reaction medium with extent of reaction). The product mixture is quantified using ^{1}H nmr spectroscopy. Schematically,

$$XabX + Yc \longrightarrow XabX + cabX + Xabc + cabc + XY$$

(X = H, Y = Cl, a = HN & half-a-benzene-ring, b = HN & half-a-benzene-ring, c = benzoic acid rest, so that XabX = the diamine, Yc = benzoic chloride, cabX & Xabc = the monoamides, cabc = the diamide, and XY = HCl) and with the definition of the following concentrations:

$[A] = [Xa-]$, $[B] = [-bX]$ (unreacted amino groups)
$[P_a] = [ca]$, $[P_b] = [bc]$ (monoamide products)

it can be shown easily that

$$r = \ln([B]/[B]_o) \,/\, \ln([A]/[A]_o)$$
$$= \ln(1 - [P_b]/[B]_o) \,/\, \ln(1 - [P_a]/[A]_o)$$

Of course, $[A]_o = [B]_o$, by necessity. For very small extents of reaction (so that $[P_a] \ll [-aX]_o$) an approximation is

$$r \approx [P_b] \,/\, [P_a].$$

This approximation is not useful for cases with $r \to 0$, however, since there $[P_a]$ will have to be substantial for $[P_b]$ to be measurable.

4. Polymer Characterization

4.1 General

The characterization of rigid-rod structures, and hence of aramides, is not easy. Rigid-rod structures are not sufficiently soluble in ordinary organic solvents for many routine methods and this provides a stumbling block in molecular level characterization. In addition, the chain rigidity creates new special problems in many techniques. We are actively pursuing new avenues of molecular level characterization. We are also progressing on the characterization of the all important liquid crystalline solutions that the polymers form.

During the first funding period a strong effort towards trifluoroacetylation of these aramides, in order to improve their solubility for characterization, had been started. Unfortunately, we have to report complete failure of this endeavour. Although it is well known that aromatic amide hydrogens are less reactive as compared to their aliphatic counterparts in such reactions, we had hoped to be able to overcome the problem. It seems, however, that absolutely no trifluorination of the substituted aramides is possible.

4.2 Rigid-Rod Behavior

Linear flexible polymer chains are viewed as forming random coils in solutions, whereas extended-chain aromatic polyamides are more nearly comparable in behavior to rigid-rods which can exist in a random array only in dilute solution. With increasing polymer concentration, the polymer chains and associated solvent arrange in parallel alignment in regions or domains. The ordered regions constitute a liquid crystalline state and form a separate phase that coexists with the initially continuous isotropic phase. Continued addition and dissolution of polymer forces more polymer into the order state until only an anisotropic phase exists. The particular type of anisotropic phase associated with aramides is often referred to as the nematic phase.

4.3 Analysis of the Liquid Crystalline Phase

In 1956 Flory first published a molecular theory of liquid crystals based on a lattice model [5]. One of the parameters predicted by this theory is the critical polymer volume fraction, v_P^*. This parameter describes the amount of polymer required at

the threshold between the initially isotropic solution and the nematic phase and is a function of the axial ratio of the polymer. Later Flory compared the results of his theory to data obtained with the aramides poly(benzamide) (PBA) and poly(p-phenyleneterephthalamide) (PPDT) [6]. As shown in Figure 4-1, the theory does an excellent job in predicting the value of v_p^*.

We have applied Flory's theory to our substituted aramides and have shown that these polymers also form liquid crystalline solutions at practically useful volume fractions. Results for single substituted polymers are shown in Figure 4-2 and those for di-substituted polymers are shown in Figure 4-3. Our preliminary experimental findings agree well with what these predictions. Work is in progress to quantitatively determine the degree of polymerization of the polymers synthesized, and thus quantitatively determine liquid crystal behavior.

4.4 Instrumental Techniques

To date only ^1H nmr and dilute solution viscometry (in 98% sulfuric acid) have been used to determine molecular level characteristics. Work has begun on determining the feasibility of the following techniques:

(1) Size Exclusion Chromatography
(2) Light Scattering
(3) ^{13}C and ^{15}N nmr
(4) Solid State nmr

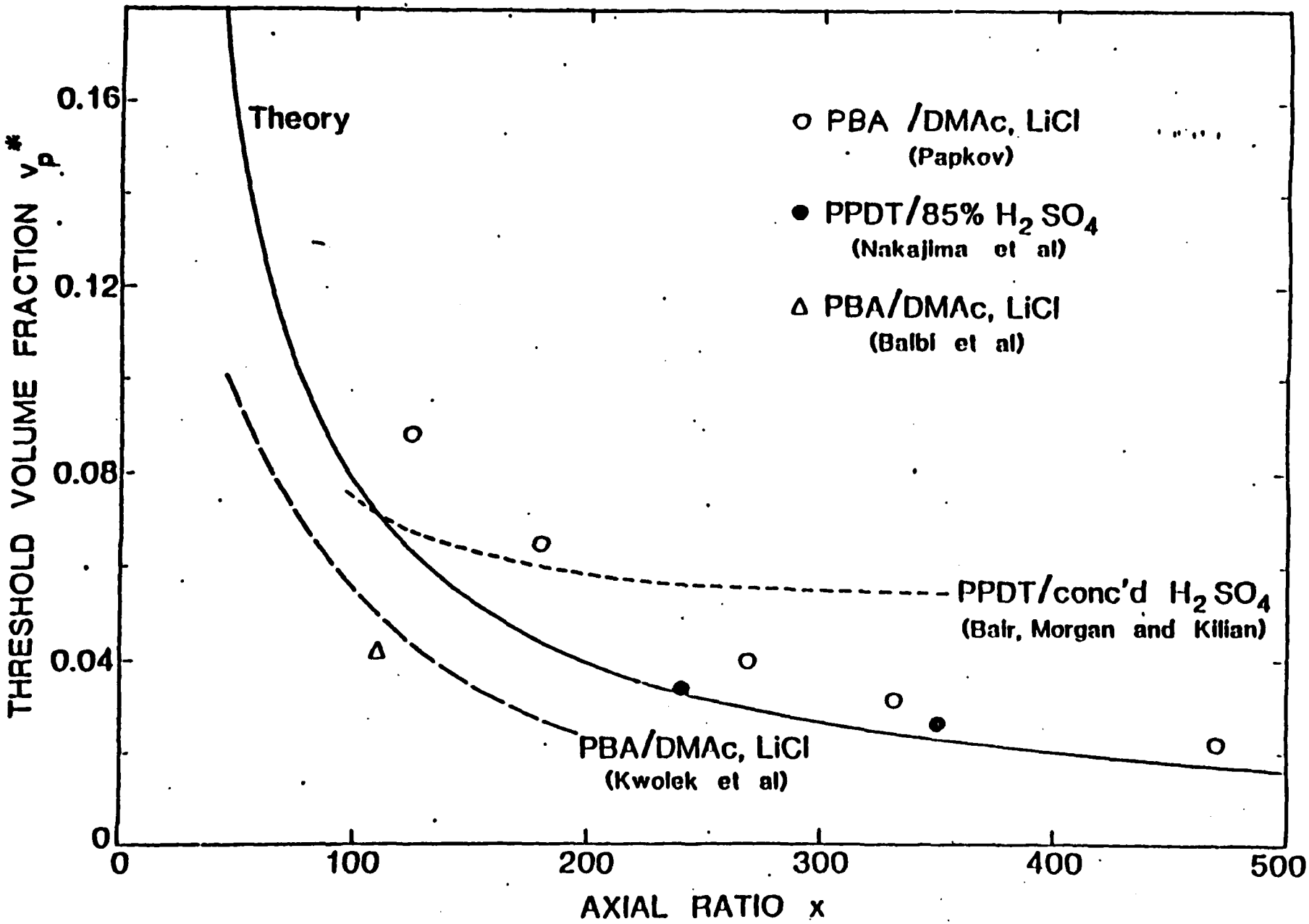


Figure 4-1 - "Molecular Theory of Liquid Crystals" by Paul J. Flory

Figure 4-2 - The Onset of a Nematic Phase for PPDT and 2-Sub-PPDT

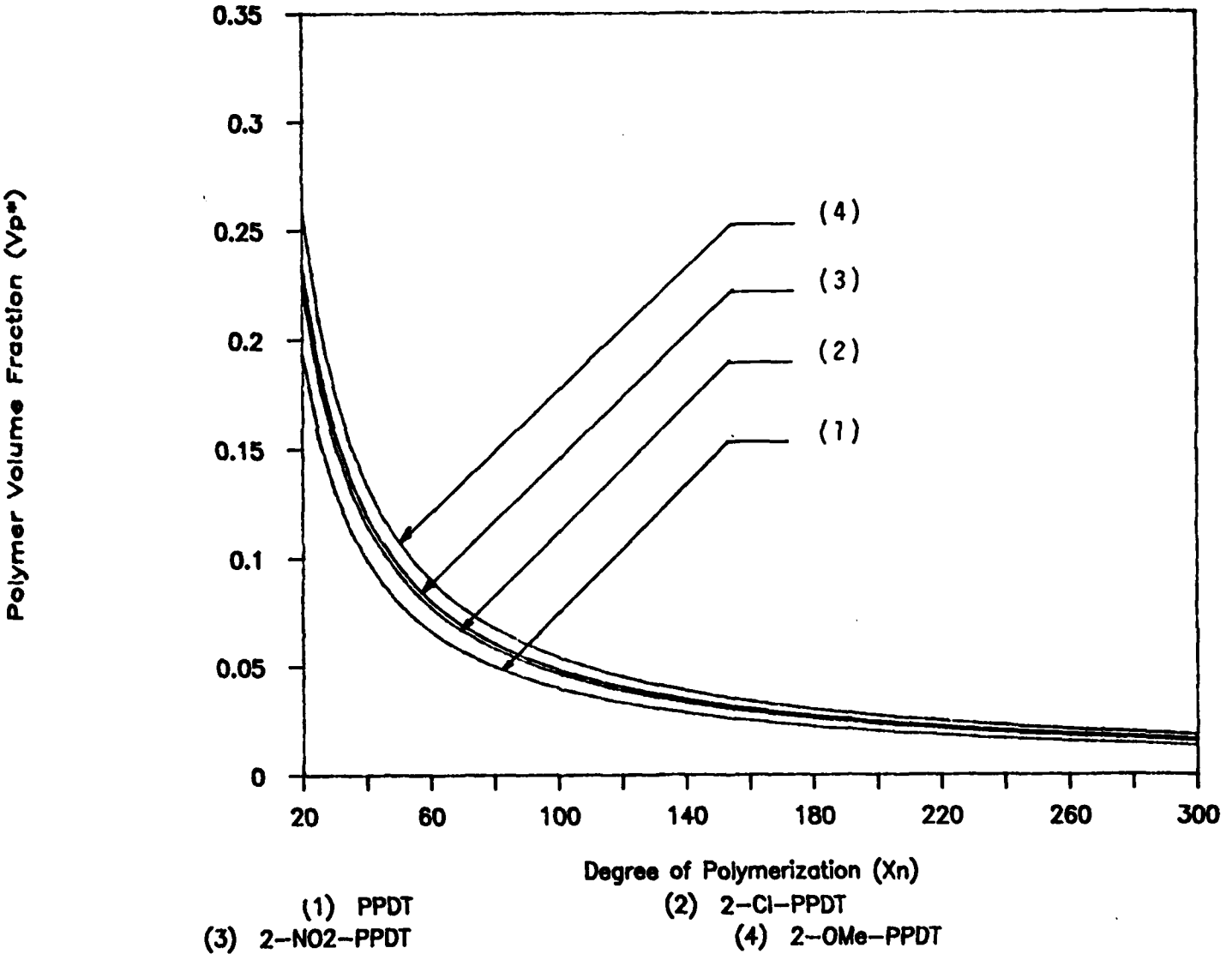
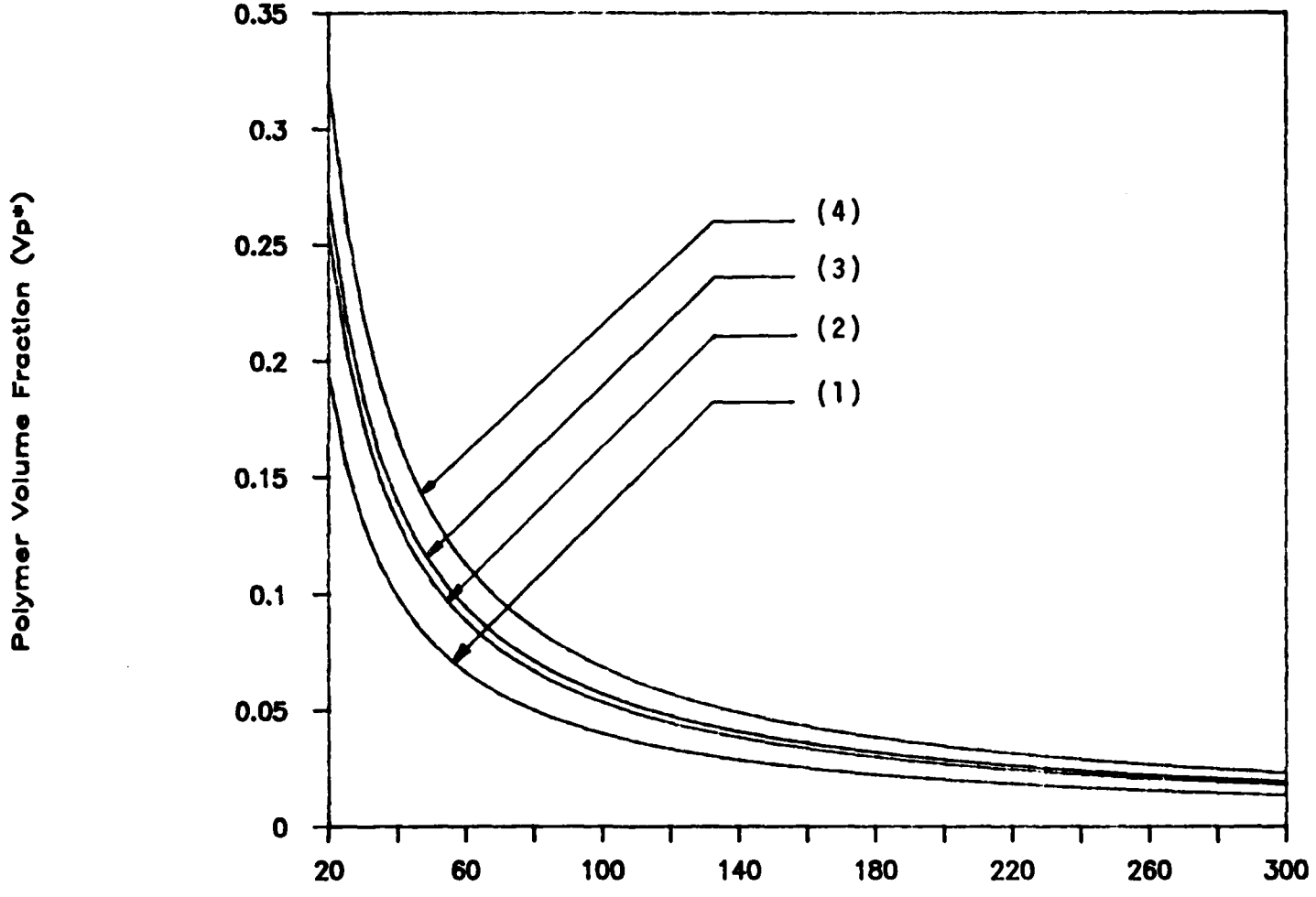


Figure 4-3 - The Onset of a Nematic Phase for PPDT and 2,6-Disub-PPDT



(1) PPDT
(2) 2,6-DiCl-PPDT
(3) 2,6-DiNO2-PPDT
(4) 2,6-DiOMe-PPDT

5. Conclusions and Recommendations

We have overcome a series of problems, some due to exaggerated optimism on our part, some serious and unknown before. To date we have developed the reaction system that allows, for the first time, to prepare extended-chain rigid-rod aramides in homogeneous reaction phase under a variety of conditions without any perceptible side reaction. The chain lengths we were able to achieve are uniformly high, sufficiently high to allow the spinning of highly oriented fibers from solution.

In addition, a set of non-symmetric monomers has been identified, prepared, purified, and shown to form high polymers, that is characterized by a very low value of r, the reactivity ratio of the two amino groups. These monomers will be the basis of the work of the coming year, and will provide the polymers with which the data necessary to conclude this project will be measured. The analytical methodology for the molecular characterization of these aramides is still not fully developed, but is currently a major focus of this project.

To date, it is clear that constitutional order has a very substantial effect on the solubility of the dichloro substituted aramide, but that it does neither diminish the thermal or chemical stability nor significantly or unexpectedly alter the concentration of polymer required for incipience of the anisotropic phase which is necessary for the production of highly oriented fibers. Optimism is in order.

We are grateful to the Office of Naval Research for providing the opportunity to conduct this research.

6. References

1. Morgan, P.W. Macromolecules 1977, 10, 1381; Kwoleck, S.L.; Morgan, P.W.; Schaefgen, J.R.; Gulrich, L.W. ibid. 1977, 10, 1390; Blair, T.I.; Morgan, P.W.; Killian, F.L. ibid. 1977, 10, 1396.

2. Pino, P.; Lorenzi, G.P.; Suter, U.W.; Casartelli, P.G.; Steinmann, A.; Bonner, F.J.; Quiroga, J. Macromolecules 1978, 11, 624; Steinmann, A., Doctoral Thesis No.6784, ETH-Zürich, 1980; Suter, U.W.; Pino, P. Macromolecules 1984 17, 2248; Schmucki, M.A.; Pino, P.; Suter, U.W. ibid. 1985, 18, 823.

3. Papkov, S.P.; Kulichikhim, V.G.; Kalmykova, V.D.; Malkin, A.; Ya, J. Polymer Sci.: Polym. Phys. Ed. 1974, 12, 1753: Pakov, S.P. Vysokomol. Soyedin. 1977, A19, 3.

4. Stubbs, F.J.; Hinshelwood, C. J. Chem. Soc. 1960, 4977.

5. Flory, P.J. Proc. Royal Soc., London 1956, A234, 74.

6. Flory, P.J. "Molecular Theory of Liquid Crystals", Adv. Polym. Sci. 1984, 59.

CONSTITUTIONAL ISOMERISM IN ARAMIDS

Werner R. Meyer, Frank N. Gentile,
James E. Gado, and Ulrich W. Suter

Department of Chemical Engineering,
Massachusetts Institute of Technology, Cambridge, MA

INTRODUCTION

Polycondensates containing "non-symmetric" monomeric units (ab) and "symmetric" monomeric units (cc), both from homobifunctional monomers, give rise to structural isomerism of the "head/tail" type (1,2). This constitutional isomerism can be controlled very well and continuously over the range of constitutional regularity $\underline{s} \rightarrow 0$ to $\underline{s} \approx 1/2$, where $\underline{s}$ is the probability of two adjacent non-symmetric monomeric units to point in the same direction, and is given by (2)

$$\underline{s} = [accb] / ([acca] + [accb] + [bccb])$$

Perfectly regular polymers containing only head-to-head and tail-to-tail enchainments exhibit a value of $\underline{s} = 0$, those that are of the head-to-tail type give $\underline{s} = 1$, and random polymers are characterized by $\underline{s} = 1/2$. Simple theoretical considerations show $\underline{s}$ to be primarily a function of the ratio of reaction rate constants of the two functional groups that form the non-symmetric monomer, i.e. of $\underline{r} = k_{bx}/k_{ax}$, and of the mode and rate of addition of the two monomers to the reaction mixture. It has been shown that, with monomers of sufficiently low $\underline{r}$, one can easily prepare in single step reactions polycondensates with structural regularities covering the entire range of $\underline{s}$ (3).

The constitutional regularity has a profound effect on the properties of polyamides (4). This can be rationalized by the fact that the more regular chains give samples of higher three-dimensional order than the more irregular polymers; packing efficiency (density) and crystallinity are a direct function of the constitutional regularity. Here we exploit this principle for the preparation of rigid-rod polymers, all analogs to poly(p-phenylene terephthalamide), but with non-symmetric diamines, in an effort to prepare materials with properties that approach that polymers' impressive performance while, at the same time, showing superior processability.

POLYMERIZATIONS

As monomers, derivatives of terephthalic acid (I) and 2-substituted or 2,6-disubstituted p-phenylenediamine (II) were used. The polycondensation must be carried out in homogeneous reaction phase, if perfect control shall be approached, and several synthetic methods were tried. They included the "phosphorylation procedure" of Higashi et al. (5), in which the diamine and the diacid are reacted in the presence of triphenyl phosphite and calcium chloride in N-methyl pyrrolidone and pyridine. While high polymers were obtained without difficulty with the unsubstituted diamine, results with the 2-monosubstituted or the 2,6-disubstituted diamine were unsatisfactory. Attempts to prepare these polymers by aminolysis of terephthalates were similarly unsuccessful.

Polymers with controllable regularity and sufficiently high degrees of polymerization were obtained by the Schotten-Baumann solution procedure. A 10:1 mixture of N-methylpyrrolidone (NMP) and tetrahydrofurane (THF) was used as solvent; NMP was chosen for its solvating power and its capacity to bind free protons, while THF was used to solvate terephthalic dichloride and to "protect" it from contact with NMP, with which it reacts readily (6) [the reaction of aromatic acid chlorides with NMP is orders of magnitude slower than that with amines, but the low concentration of amine during slow addition of the diamine in one of the procedures employed makes the reaction with NMP dominant]. The reactions were carried out at room-temperature under strict exclusion of moisture in inert atmosphere.

The degree of constitutional order in the polymers can be determined (in some cases only qualitatively) by observation of the amide proton ^1H nmr spectra. Table 1 summarizes the results of synthesis.

TABLE 1 : Polymers by Solution Schotten-Baumann Reaction

I + 2-Substituted II

Substituent	Order[a]	η_{inh}[b]
$-CH_3$	random	0.20 (25°C)
	ordered	0.18 (25°C)

I + 2,6-Disubstituted II

Substituents	Order[a]	η_{inh}[b]
$-CH_3$	random	0.32 (25°C)
	ordered	0.27 (25°C)
$-Cl$	random	0.29 (30°C)
	ordered	0.33 (30°C)

a) "random": $\underline{s} \approx 0.5$, obtained by very slow addition of non-symmetric diamine to terephthaloyldichloride; "ordered": $\underline{s} \rightarrow 0$, obtained by very slow addition of the terephthaloyldichloride to the diamine.
b) in 98% sulfuric acid, at 1 mg/ml.

The properties of the resulting polymers differ clearly for different constitutional regularity. The solubility in dimethylsulfoxide/lithium chloride, for instance, is larger in the less ordered samples by a factor of two to three [by "solubility" we mean the maximum concentration giving an apparently homogeneous solution at 100°C]: for the polymer formed from the mono-methyl diamine the solubilities are 67 and 21 mg/ml, respectively, for the dimethyl diamine chains they are 41 and 22 mg/ml, respectively, and for the dichloro diamine macromolecules the corresponding values are 58 and 20 mg/ml. Kevlar™, for comparison, exhibits a value of 10 mg/ml.

The thermal stabilities of all these polymers is comparable to that of poly(p-phenylene terephthalamide).

ACKNOWLEDGEMENT

It is a pleasure to acknowledge support by the Office of Naval Research under contract number N00014-85-K-0161.

REFERENCES

(1) Preston, J., Smith, R. J. Polym. Sci., Part B 1966, 4, 1033;
Pino, P., Casartelli, P.G., Quiroga, J.A., Lorenzi, G.P., Int. Symp. Macromol. Chem., Madrid, Prepr. 1974, 1, 255;
Korshak, V.V., Vinogradova, S.V., Kuchanov, S.I., Vasnev, V.A., Markova, G.D., Tarasov, A.I. Polym. Sci. USSR 1974, 16, 1302.
(2) Suter, U.W., Pino, P., Macromolecules 1984, 17, 2248.
(3) Schmucki, M.A., Pino, P., Suter, U.W., Macromolecules, 1985, 18, 823.
(4) Steinmann, A., Suter, U.W., Pino, P. , Int. Symp. Macromol. Chem., Florence, Prepr. 1980, 2, 228;
Steinmann, A., Doctoral Thesis No.6784, ETH-Zürich, 1980.
(5) Yamazaki, N., Matsumoto, M., Higashi, F., J. Polym. Sci.: Polym. Chem. Ed. 1975, 13, 1373;
Higashi, F., Ogata, S., Aoki, Y., J. Polym. Sci.: Polym. Chem. Ed. 1982, 20, 2081;
Higashi, F., Ogata, S., Akiyama, N., J. Polym. Sci.: Polym. Chem. Ed. 1981, 21, 913.
(6) Savinov, V.M., Sokolov, L.B., Polym. Sci. USSR, 1966, 7, 851.

FOLD

FOLD

Folio

END

10-86

DTIC